

Poly(methyl methacrylate), General

Synonym:

Poly(methyl 2-methyl-2-propenoate)
Poly[1-(methoxycarbonyl)-1-methyl ethylene]
Acrylic
PMMA

Monomers:

Methyl methacrylate

Related Polymers:

Polymethacrylates-General
Moulding and Extrusion Compounds
Cast Sheet (rods and tubes)
Extruded Sheet
Butyl methacrylate copolymer

Material Class

Thermoplastic

Polymer Type:

acrylic

CAS Reg. No.:

9011-14-7 [general]; 25188-98-1 [isotactic]; 25188-97-0 [syndiotactic]

Molecular Formula:

$(C_5H_8O_2)_n$

Fragment:

C₅H₈O₂

Mol. Weight:

MN 300000-600000 (cast material); 100000-200000 (moulded or extruded material); 252000 (GPC determined); MW 481000 (GPC determined); MZ 766000 (GPC determined); MZ +1 1196000 (GPC determined)

Additives:

PMMA materials may contain residual monomer or processing additives. Typical additives used in the manufacture of **PMMA** by suspension polymerisation (usually for moulding and extrusion compounds) include suspending agents, buffering agents, chain transfer agents (to control MW), lubricants and emulsifier. A number of additives may be blended with **PMMA**, perhaps the most important being dyes and pigments. Listings of commonly used colorants for **PMMA** have been reported. [1]

Sucrose-based additives improve heat stability. Plasticisers are sometimes used with **PMMA**, e.g. in moulding compositions to enhance the melt flow. Levels vary from 1-50%; 5% is typical.

Lubricants reduce heat dissipation during machining or polishing.

Some commercial grades contain uv absorbers (290-350 nm). This both screens the user from sunburn, e.g. in glazing applications, and protects the polymer against long term degradation from light. Typical levels are in the range 0.001-2%.

Alumina hydrate is used as a flame-retardant filler in some forms of **PMMA** used for bathroom fittings, kitchen worktops and 'synthetic marble'.

Fillers and reinforcements are not often used although chalk is sometimes incorporated, e.g. for opaque illuminated panels in advertising displays. **PMMA** can be reinforced, e.g. with glass fibre, polyethylene, Kevlar or carbon to ensure high mechanical strength at temps. around 100°.

Polystyrene (0.2-5%) may be added as an opalescent.

Rubber particles increase toughness

Tacticity:

Although nominally atactic, conventionally produced **PMMA** is more syndiotactic than atactic.

Differences in the adsorption behaviour of atactic and tactic polymers have been reported: isotactic **PMMA** is absorbed onto silica (from acetonitrile soln.) whereas atactic **PMMA** is not. [4]

Stereoregular polymers may be prod. in soln. by use of anionic catalysts, e.g. organolithium compounds or Grignard reagents. Isotactic polymers tend to be prod. in non-polar solvents and syndiotactic in polar solvents. The change in composition of the product polymer in a series of reactions carried out in various toluene/dimethoxyethane mixtures using *n*-butyl lithium as initiator at -30° has been reported. [5]

Stereoregular **PMMA** can be made by living polymerisation in toluene using *tert*-butyl MgBr (for isotactic) or *tert*-butyl lithium aluminium alkyl (for syndiotactic). Living polymerisation also allows the preparation of star and comb-like polymers with stereoregular main and side chains, e.g. isotactic main chain and syndiotactic side chain [13,14]

Morphology:

Commercial grades are normally amorph.

Isotactic: orthorhombic a 41.96Å, b 24.34Å, c 10.50Å, α 92.9°, β 88.2°, γ 90.6° containing eight double-strand 10/1 helices per cell. [6,7,8] Repeat unit volume 87-89 cm³ mol⁻¹ [9]; 89.3 cm³ mol⁻¹. [10]

The head-to-head polymer has been reported [11]

Identification:

Contains only C, H and O. The surface of any acrylic plastic is immediately fogged or crazed by Me₂CO

General Info:

PMMA may be fractionated by means of supercritical fluid chromatography. [3] Commercially the most important member of the acrylate/methacrylate group of polymers, **PMMA** was first introduced in 1936 and is available as cast and extruded sheet, tubes, rods, powders, pellets, solns, dispersions and emulsions. In addition to its use in sheet form, **PMMA** is also suitable for many extrusion and moulding applications, coating and surface treatments and has many industrial uses.

It is non-toxic, odourless and tasteless. Nothing is extracted from **PMMA** by oil or water.

PMMA may be coloured to give transparent, translucent or opaque forms. It is possible to texture the surface of **PMMA** products during moulding or by later embossing and products may be further decorated by spray-painting, vacuum-metallising, hot stamping etc.

It is a clear, colourless, hard, brittle, fairly rigid material which can be drilled, carved or sawn and has exceptional optical clarity and resistance to degradation by uv light. The hardest and most heat resistant **PMMA** materials are the cast sheet products, followed by continuous cast materials, then the extruded or moulded products.

Its total internal reflection permits a wide light beam to be transmitted through long lengths of **PMMA** and around corners with little loss provided that the radius of curvature of the sheet or rod is three times its thickness.

Has good electrical insulating props. at low frequencies. Above its glass transition temp. **PMMA** is tough, pliable, extensible and easily bent or formed into complex shapes; at high temps., however, it is very susceptible to depolymerisation.

It is a polar material and will absorb some moisture but is resistant to alkali, detergent, oils and dilute acids.

Although **PMMA** has comparatively limited impact resistance this can be improved by copolymerisation, e.g. Butyl acrylate/MMA (see [Acrylic/methacrylic copolymers](#)) or acrylonitrile/MMA (see [Acrylonitrile-methyl acrylate copolymer](#)), or by blending e.g. with Poly(*n*-butyl acrylate) (see [Poly\(*n*-butyl methacrylate\)](#)) or a butadiene copolymer.

PMMA has low flammability, a high melt viscosity, low resistance to creep at temps. only a little above room temp., poor solvent resistance and a comparative lack of abrasion resistance.

Volumetric and Calorimetric Properties

Density:

No.	Value	Note
1	1.15 – 1.23 ²⁵ g/cm ³	[2,6,18,19,22,23]
2	1.17 ²⁵ g/cm ³	amorph. [2,21]
3	1.19 ²³ g/cm ³	cast and extruded grades, 50% relative humidity, ISO 1183 [20]
4	1.19 ³⁰ g/cm ³	syndiotactic [18]
5	1.19 ³⁰ g/cm ³	conventional [18,19,20]
6	1.21 – 1.22 ³⁰ g/cm ³	isotactic [6,18]
7	1.23 ²⁵ g/cm ³	cryst. [2]

Thermal Expansion Coefficient:

No.	Value	Note
1	0.000048 – 0.00008 K ⁻¹ [L]	impact modified, ASTM D696 [24]
2	0.00005 – 0.00006 K ⁻¹ [L]	general purpose, cast sheet, ASTM D696 [24]
3	0.00007 K ⁻¹ [L]	cast and extruded grades, 0-50°, DIN 53752-A [20]
4	0.000225 – 0.000295 K ⁻¹ [V]	T < T _g , 1 atm, free radical polymerisation [26]
5	0.00053 – 0.000575 K ⁻¹ [V]	T > T _g , 1 atm, free radical polymerisation

Volumetric Properties General:

Molar volumes at 25° [2]: 56.1 cm³ mol⁻¹ van der Waals, 86.5 cm³ mol⁻¹ glassy, 81.8 cm³ mol⁻¹ cryst.

Equation of State:

Tait, Bruce-Hartmann, Sanchez and Lacombe, Spencer-Gilmore and Smka-Somcynsky equation of state information has been reported [27,28,29,30,31,32,33]

Thermodynamic Props General:

Thermal conductivity varies with both temp. and pressure although at ordinary pressure the variation is quite small. Control over thermomechanical props. can be improved by the addition of low MW poly(butyl methacrylate) or poly(butyl-co-methyl methacrylate). [35].

Molar heat capacity data for amorph. PMMA has been reported [42]

Latent Heat of Cryst:

Enthalpy of melting 9.6 kJ mol⁻¹. [2] Entropy data for a range of temps. and pressures have been reported. [28]

Entropy, enthalpy and Gibbs free energy data for temps. -263 – -13° have been reported in a graphical form [36]

Thermal Conductivity:

No.	Value	Note
1	0.15 – 0.2 W/m K	[2]
2	0.15 – 0.161 W/m K	-50° [37]
3	0.17 W/m K	clear cast sheet, NBN B62-202 [41]
4	0.19 W/m K	cast and extruded grades, DIN 4701 [20]
5	0.197 W/m K	0.00047 cal (s cm °C) ⁻¹ , 35° [38,39]
6	0.25 W/m K	100° [40]

Specific Heat Capacity:

No.	Value	Note
1	1.38 kJ/(kg °C) [P]	solid, 25° [2]
2	1.47 kJ/(kg °C) [P]	cast and extruded grades [20]
3	1.8 kJ/(kg °C) [P]	liq. 25° [2]

Melting Temperature:

No.	Value	Note
1	72°C	emulsion polymerisation, refractometric method [43]
2	160°C	isotactic [18]
3	>200°C	min., syndiotactic [18]

Glass Transition Temperature:

No.	Value	Note
1	41.5°C	isotactic 95%, atactic 5% [46]
2	43 – 45°C	isotactic [18,44,45]
3	54.3°C	isotactic 73%, atactic 16%, syndiotactic 11% [45]
4	61.6°C	isotactic 62%, atactic 20%, syndiotactic 18% [45]
5	80 – 100°C	impact-modified, ASTM D3418 [24]
6	85 – 105°C	ASTM D3418 [24]
7	90 – 105°C	cast sheet, ASTM D3418 [24]
8	104°C	isotactic 6%, atactic 30%, syndiotactic 56% [46]
9	105°C	conventional [26]
10	114.2°C	isotactic 10%, atactic 31%, syndiotactic 59% [45]
11	115°C	syndiotactic [18]
12	119.5°C	isotactic 10%, atactic 20%, syndiotactic 70% [46]
13	125.6°C	isotactic 9%, atactic 36%, syndiotactic 64% [45]
14	160°C	syndiotactic [44]

Deflection Temperatures:

No.	Value	Note
1	71 – 102°C	1.82 MPa, cast sheet, ASTM D648 [54]
2	74 – 99°C	1.82 MPa, impact-modified, ASTM D648 [54]
3	74 – 113°C	0.455 MPa, cast sheet ASTM D648 [54]
4	74 – 105°C	1.82 MPa, ASTM D648 [24]
5	76 – 106°C	1.82 MPa, MEC, ASTM D648, DIN 53461, ISO R-75 [22,23,46]
6	79 – 107°C	0.455 MPa, ASTM D648 [24]
7	82 – 102°C	0.455 MPa, impact-modified, ASTM D648 [54]
8	85 – 95°C	1.82 MPa, moulding compound, ASTM D648 [46]
9	88 – 102°C	ISO 75A [23]
10	90°C	1.8 MPa, extruded, ISO 75 [20]
11	91 – 106°C	ISO 75B [23]
12	95°C	0.45 MPa, extruded, ISO 75 [20]
13	100°C	1.82 MPa, sheet, ASTM D648 [46]
14	102°C	cast, ISO 75A [41]
15	105 – 107°C	1.8 MPa, cast, ISO 75 [20]
16	108°C	1.82 MPa, 75% glass fibre, pultrusion [47]
17	110°C	1.82 MPa, 75% glass fibre, pultrusion, post formed [47]
18	113°C	carbon fibre, pultruded [48]
19	113 – 115°C	0.45 MPa, cast, ISO 75 [20]
20	116°C	carbon fibre, pultruded and postformed [48]
21	117°C	Kevlar fibre, pultruded [48]
22	118°C	1.82 MPa, 58% carbon fibre, pultrusion [47]
23	119°C	Kevlar fibre, pultruded and postformed [48]

Vicat Softening Point: